

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B22D 11/10, 11/07, C21C 7/076		A1	(11) International Publication Number: WO 96/32216 (43) International Publication Date: 17 October 1996 (17.10.96)
(21) International Application Number: PCT/GB96/00568 (22) International Filing Date: 12 March 1996 (12.03.96) (30) Priority Data: 08/421,151 10 April 1995 (10.04.95) US		(81) Designated States: AU, CA, CN, JP. Published <i>With international search report.</i>	
(71) Applicant: FOSECO INTERNATIONAL LIMITED [GB/GB]; 285 Long Acre, Nechells, Birmingham B7 5JR (GB). (72) Inventors: PHILLIPS, Royston, John; 19295 Timber Creek Circle, Strongsville, OH 44136 (US). DIEHL, Spencer, Clarke; 25127 Sunset Oval, North Olmsted, OH 44070 (US). (74) Agent: EYLES, Winifred, Joyce; Foseco International Limited, Burmah Castrol Group Patents Dept., 285 Long Acre, Nechells, Birmingham B7 5JR (GB).			

(54) Title: MOULD FLUXES FOR USE IN THE CONTINUOUS CASTING OF STEEL

(57) Abstract

A granular mould flux for use in the continuous casting of steel, and particularly ultra low carbon steels, comprises refractory metal oxide, one or more fluxing agents, an expanding agent such as expandable graphite, expandable perlite or expandable vermiculite, carbon black, manganese dioxide and starch. The granules are preferably spherical granules of 0.1 mm to 1 mm in diameter. A preferred composition contains sodium carbonate and/or lithium carbonate which act binders in addition to being fluxing agents.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

- 1 -

**MOULD FLUXES FOR USE IN THE
CONTINUOUS CASTING OF STEEL**

This invention relates to mould fluxes for use in the continuous casting of steel, particularly ultra low carbon steel.

In the continuous casting of steel a mould flux is generally added to the surface of the molten steel in the mould. The flux provides lubrication between the mould wall and the steel, it reduces the loss of heat from the surface of the steel, it protects the surface from oxidation and it may remove impurities such as alumina from the steel.

As granules evolve much less dust compared with powder mould fluxes used in the continuous casting of steel, are often used in the form of granules which may be produced by, for example, spray-drying of the flux constituents. The excellent flowability of granules makes them particularly suitable for automatic feeding to the mould, for example, using a DAPSOL™ feeder. However, once the flux is in the mould, the flowability of the granules becomes a disadvantage since the granules tend to find their own level under high rates of flow of steel into the mould and the surface of the steel may become exposed in the corners of the mould.

It has been found that the above problem can be alleviated if the granules contain a minor amount of an expandable material which will expand under the action of heat and will cause the granules to break down into powder on the surface of the steel. It has also been found that spherical granules yield the best results, that the expandable material (particularly acid treated graphite) should have a particular

- 2 -

size and that particular binders should be utilised in order to obtain the best results.

In the continuous casting of ultra low carbon (ULC) steel, the insulating properties of the mould fluxes are especially critical and carbon pickup must be minimised.

It has now been found that spherical granules can be used for ULC steels even though the conventional wisdom is that granules do not insulate as well as powders and, therefore, are not suitable for use with ULC steels.

According to the invention there is provided a granular mould flux comprising refractory metal oxide, one or more fluxing agents, an expanding agent, carbon black, manganese dioxide and starch.

According to a further feature of the invention there is provided a method of continuously casting molten steel in a mould, the method comprising adding to the mould prior to, during or after teeming of the molten steel a granular mould flux comprising refractory metal oxide, one or more fluxing agents, an expanding agent, carbon black, manganese dioxide and starch.

In the preferred method the steel is ultra low carbon steel.

The refractory metal oxide is preferably made up of calcium oxide and silica but alumina and/or magnesia may also be present. Materials such as blast furnace slag which contains calcium oxide, silica and alumina, or feldspar (sodium potassium aluminium silicate)

- 3 -

which contains alumina and silica may be used as a source of refractory metal oxides.

Wollastonite, which contains calcium oxide and silica, is a particularly useful component since it is capable of absorbing appreciable amounts of alumina from the steel into the flux without significantly affecting the viscosity or melting point of the flux. The wollastonite component may be, for example, a synthetic or natural calcium monosilicate (which may contain very small quantities of iron oxide and/or alumina), or it may be calcium monosilicate in solid solution with at least one of silica, calcium oxide and alumina, for example, a solid solution containing pseudo-wollastonite or rankinite.

The fluxing agent may be, for example, one or more of sodium carbonate (soda ash), potassium carbonate, lithium carbonate, barium carbonate, sodium fluoride, aluminum fluoride, potassium fluoride, cryolite, fluorspar and olivine. The fluxing agent reduces the melting point of the flux and by the selection of particular fluxing agents and amounts the variation of the viscosity of the flux with temperature can be controlled.

The expanding agent is preferably acid-treated or expandable graphite but the expanding agent may be, instead of acid-heated graphite, expandable perlite or expandable vermiculite. The expanding agent is preferably present in an amount of 0.3% to 1.5%, most desirably 0.3 to 1% by weight based on the weight of the flux and is preferably expandable graphite.

The starch functions as a binder but if desired other binders may also be used in addition to the starch.

- 4 -

The additional binder may be any suitable binder which will maintain the integrity of the granules from manufacture through storage, transport and use up to the point of expansion of the expanding agent when it is necessary for the granules to disintegrate back into the original powder form. Examples of suitable binders include resins, gums such as a polysaccharide gum and carbohydrate materials such as molasses.

Sodium carbonate (soda ash) and/or lithium carbonate which, are fluxing agents, can also function as binders and as such are highly desirable in the granular flux of the invention. At least 4% soda ash, or at least 2% lithium carbonate, or a combination of at least 2% soda ash and at least 1% lithium carbonate, are typically used. Most desirably the binder content of the granular mould flux comprises between about 8 to 14% by weight soda ash, or between about 4 to 7% by weight lithium carbonate, or a combination of soda ash and lithium carbonate wherein double the percentage of lithium carbonate, plus the percentage of soda ash, is between about 8 to 14% by weight. For example, one particularly desirable combination for the binder is about 10% soda ash and about 1% lithium carbonate. This binding mechanism for producing the granular mould flux has proven more effective than using some organic binders in terms of granule strength as well as absence of odour. The size of the granules produced by spray drying such a composition is preferably about 0.2 - 0.5 mm (200 - 500 microns).

The starch binder in the granular flux of the invention causes the carbon black to migrate to the surface of the granules thus improving the efficiency of the carbon black addition, reducing slag rim, improving thermal insulation and reducing carbon pickup by the steel.

- 5 -

The manganese dioxide oxidises carbon, and reduces carbon pickup by the steel, allowing a higher carbon content flux to be used and providing improved thermal insulation and less slag rim.

The amount of starch will usually be 0.1 to 1.0% by weight, for example, 0.3 to 0.7% by weight, typically about 0.5% by weight and the amount of manganese dioxide will usually be 1 to 5% by weight, for example, about 2 to 4% by weight, typically about 3% by weight.

The flux may also contain a light-weight refractory material such as expanded perlite, expanded vermiculite, or pumice, to lower the overall density of the flux.

The flux may also contain a carbonaceous material, (in addition to carbon black and any expandable graphite which may be present as the expanding agent), such as charcoal, coke, anthracite or graphite, to control the melting rate and sintering characteristics of the flux.

The amount of such carbonaceous material may be, for example, up to 6% by weight, preferably up to 3% by weight.

The flux will usually contain by weight:-

- 6 -

45.0 - 90.0%	Refractory metal oxide
10.0 - 50.0%	Fluxing agent
0.3 - 1.5%	Expanding agent
0.1 - 1.5%	Carbon black
1.0 - 5.0%	Manganese dioxide
0.1 - 1.0%	Starch
0 - 14.0%	Sodium carbonate
0 - 7.0%	Lithium carbonate
0 - 10.0%	Light-weight refractory material
0 - 6.0%	Carbonaceous material (other than carbon black and any expandable graphite present as expanding agent).

The granular mould flux of the invention is preferably in the form of spherical granules. Spherical granules have the best properties in terms of chemical uniformity and cold flowability and also have suitable insulating ability. However, conventional spherical granules in the past have not been as forgiving in the mould as powders during turbulent conditions. During turbulent conditions the narrow face is particularly disturbed by rolling and level variation and spherical granules tend to run down toward the lower levels due to their good flowability. This can result in exposing liquid flux or even steel near the narrow face. However, because of the expanding agent according to the invention, as well as the reduced average particle size of the spheres, the permeability of the flux is reduced thereby improving its insulating properties and the cold flowability is reduced, the net result being that the material can be used successfully during submerged entry shroud (SEN) and tundish changes without the tendency to form steel floaters.

The spherical granules may be produced by a method such as pan granulation but they are preferably produced by spray drying an aqueous slurry of a mixture of the flux constituents, typically about 60% solids. The granules may be in a size range as broad as from 0.1 mm to 1 mm in diameter but preferably are 0.2 to 0.5 mm (200 to 500 microns) in diameter.

The application rate of the mould flux to the mould will usually be in the range of 0.3 kg/ton to 1.1 kg/ton of steel cast which is substantially the same as for conventional fluxes.

In the casting of ULC steels, carbon pick-up is minimised by using mould fluxes which have a lower carbon content compared with fluxes used for the casting of other steels, and this may result in reduced thermal insulation properties and increased slag rim formation. Since conventional granules do not insulate as well as powders, granules are not normally used for casting ULC steels.

The granular mould flux of the invention is particularly suitable for the casting of ULC steels. The expanding agent causes the flux to break down into powder, thus improving metal coverage during turbulent conditions. The manganese dioxide oxidises carbon contained in the flux and reduces carbon pick-up by the steel, thus permitting a higher carbon content in the flux and giving improved insulation properties and less slag rim production. The starch causes the carbon black to migrate to the surface of the granules, thus improving the efficiency of the carbon black in reducing slag rim production and providing improved insulation properties.

- 8 -

As stated previously the granular mould flux of the invention breaks down in contact with the steel in the mould producing a powder layer of flux on the surface and preventing exposure of the steel in the mould corners. Additionally, the granular mould flux of the invention retains the advantages of known granular mould fluxes such as greater homogeneity compared with powder flux compositions, low dust production and excellent flowability for ease of automatic application.

The following examples will serve to illustrate the invention:

EXAMPLE 1

% by weight

Calcium silicate	21.5
Carbon black	0.8
Blast furnace slag	28.2
Calcium fluoride	12.3
Olivine	6.1
Sodium potassium aluminum silicate	11.8
Starch	0.5
Manganese dioxide	2.8
Lithium carbonate	1.2
Sodium carbonate	6.1
Polysaccharide gum	0.1
Strontium carbonate	7.6
Expandable graphite	1.0

- 9 -

EXAMPLE 2

	<u>% bv weight</u>
Calcium silicate	21.9
Carbon black	0.8
Blast furnace slag	31.4
Calcium fluoride	11.6
Magnesite	2.4
Sodium potassium aluminum silicate	8.4
Starch	0.6
Manganese dioxide	3.6
Lithium carbonate	1.7
Sodium carbonate	3.4
Polysaccharide gum	0.1
Expandable graphite	0.8
Soda lime glass	13.3

Spherical granules of size 0.2 mm to 0.5 mm in diameter were produced from the compositions of Examples 1 and 2 by spray drying an aqueous slurry of the compositions. The granules were used as mould fluxes in the continuous casting of ultra low carbon steel.

- 10 -

CLAIMS

1. A granular mould flux comprising refractory metal oxide, one or more fluxing agents and an expanding agent characterised in that the flux also contains carbon black, manganese dioxide and starch.
2. A granular mould flux according to Claim 1, characterised in that the refractory metal oxide content is made up of calcium oxide and silica and optionally alumina and/or magnesia.
3. A granular mould flux according to Claim 1 or Claim 2, characterised in that the fluxing agent is one or more of sodium carbonate, potassium carbonate, lithium carbonate, barium carbonate, sodium fluoride, aluminium fluoride, potassium fluoride, cryolite, fluorspar and olivine.
4. A granular mould flux according to any one of Claims 1 to 3, characterised in that the expanding agent is expandable graphite, expandable perlite or expandable vermiculite.
5. A granular mould flux according to any one of Claims 1 to 4, characterised in that the flux contains by weight:-



- 11 -

45.0 - 90.0%	Refractory metal oxide
10.0 - 50.0%	Fluxing agent
0.3 - 1.5%	Expanding agent
0.1 - 1.5%	Carbon black
1.0 - 5.0%	Manganese dioxide
0.1 - 1.0%	Starch
0 - 14.0%	Sodium carbonate
0 - 7.0%	Lithium carbonate
0 - 10.0%	Light-weight refractory material
0 - 6.0%	Carbonaceous material (other than carbon black and any expandable graphite present as expanding agent).

6. A granular mould flux according to Claim 5, characterised in that the expanding agent content is 0.3 to 1.0% by weight.
7. A granular mould flux according to Claim 5 or Claim 6, characterised in that the manganese dioxide content is 2.0 to 4.0% by weight.
8. A granular mould flux according to any one of Claims 5 to 7 characterised in that the starch content is 0.3 to 0.7% by weight.
9. A granular mould flux according to any one of Claims 5 to 8, characterised in that the sodium carbonate content is 2.0 to 14.0% by weight.
10. A granular mould flux according to Claim 9, characterised in that the sodium carbonate content is 8.0 to 14.0% by weight.

- 12 -

11. A granular mould flux according to any one of Claims 5 to 10, characterised in that the lithium carbonate content is 1.0 to 7.0% by weight.
12. A granular mould flux according to Claim 11, characterised in that the lithium carbonate content is 4.0 to 7.0% by weight.
13. A granular mould flux according to any one of Claims 5 to 12, characterised in that twice the lithium carbonate content plus the sodium carbonate content is in the range of 8.0 to 14.0% by weight.
14. A granular mould flux according to any one of Claims 5 to 13, characterised in that the light-weight refractory material is expanded perlite, expanded vermiculite or pumice.
15. A granular mould flux according to any one of Claims 9 to 14, characterised in that the carbonaceous material is charcoal, coke, anthracite or graphite.
16. A granular mould flux according to any one of Claims 9 to 15, characterised in that the flux contains a binder in addition to the starch and any sodium carbonate and/or lithium carbonate which may be present.
17. A granular mould flux according to Claim 16, characterised in that the additional binder is a resin, a gum or a carbohydrate material.

- 13 -

18. A granular mould flux according to any one of Claims 1 to 17, wherein the granules are spherical granules of 0.1 mm to 1 mm in diameter.
19. A granular mould flux according to Claim 18, wherein the granules are spherical granules of 0.2 mm to 0.5 mm in diameter.
20. A method of continuously casting molten steel in a mould, the method comprising adding to the mould prior to, during or after teeming of the molten steel, a mould flux comprising a refractory metal oxide, one or more fluxing agents, an expanding agent, carbon black, manganese dioxide and starch.
21. A method according to Claim 20, wherein the steel is ultra low carbon steel.

INTERNATIONAL SEARCH REPORT

Internal Application No

PCT/GB 96/00568

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 B22D11/10 B22D11/07 C21C7/076

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 B22D C21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 137 734 (FOSECO INTERNATIONAL LTD.) 17 April 1985 see page 8 - page 9; claims 1-12	1-4,20, 21
A	---	5-19
Y	WO,A,95 05911 (FOSECO INTERNATIONAL LTD.) 2 March 1995 see claims 1-10; examples 1,2	1-4,20, 21
A	---	5-19
Y	GB,A,1 514 185 (ROBSON REFRACTORIES LTD.) 14 June 1978 see page 1, line 50 - line 65 see page 2, line 2 - line 39; examples 1,2 ---	1-4,20, 21
	-/-	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *'A' document defining the general state of the art which is not considered to be of particular relevance
- *'B' earlier document but published on or after the international filing date
- *'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *'O' document referring to an oral disclosure, use, exhibition or other means
- *'P' document published prior to the international filing date but later than the priority date claimed

*'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

*'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

*'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

*'A' document member of the same patent family

3

Date of the actual completion of the international search

18 June 1996

Date of mailing of the international search report

02.07.96

Name and mailing address of the ISA
 European Patent Office, P.B. 5818 Patentstaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+31-70) 340-3016

Authorized officer

Bombeke, M

INTERNATIONAL SEARCH REPORT

Intern. J Application No
PCT/GB 96/00568

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE,A,19 58 537 (EITEL, HANS-JOACHIM) 24 June 1971 see page 1 - page 3; claims 1-3	1-4,20, 21
A	---	5-17
A	EP,A,0 510 842 (FOSECO INTERNATIONAL LTD.) 28 October 1992 see page 2, line 40 - line 54; claims 1,4-10,13	1-18
A	---	1-21
A	DE,A,35 37 281 (VEB BANDSTAHLKOMBINAT) 21 August 1986 see page 5 - page 7	1-21
A	---	1-21
A	RESEARCH DISCLOSURE, vol. 142, no. 34694, February 1993, EMSWORTH GB, XP000360723 "Tundish cover layer" see whole document	1-21
A	---	1-21
	GB,A,2 066 859 (FOSECO TRADING AG) 15 July 1981 see page 2	-----

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No

PCT/GB 96/00568

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-137734	17-04-85	AU-B-	561941	21-05-87
		AU-B-	3298684	28-03-85
		CA-A-	1216500	13-01-87
		DE-A-	3473124	08-09-88
		JP-C-	1813161	27-12-93
		JP-B-	3079100	17-12-91
		JP-A-	60087960	17-05-85
		US-A-	4561912	31-12-85
-----	-----	-----	-----	-----
WO-A-9505911	02-03-95	AU-B-	7388494	21-03-95
-----	-----	-----	-----	-----
GB-A-1514185	14-06-78	NONE		
-----	-----	-----	-----	-----
DE-A-1958537	24-06-71	NONE		
-----	-----	-----	-----	-----
EP-A-510842	28-10-92	CA-A-	2067067	26-10-92
		US-A-	5240492	31-08-93
-----	-----	-----	-----	-----
DE-A-3537281	21-08-86	NONE		
-----	-----	-----	-----	-----
GB-A-2066859	15-07-81	CA-A-	1136528	30-11-82
		DE-A-	3045021	27-08-81
		FR-A,B	2471236	19-06-81
		JP-A-	56089372	20-07-81
		SE-B-	445432	23-06-86
		SE-A-	8008292	31-05-81
-----	-----	-----	-----	-----